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Structure of weakly charged polyelectrolytes at a solid-liquid interface

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Abstract. — The equilibrium structure of a monolayer formed by long polyelectrolyte chains adsorbed at the interface between a charged surface and a dilute polyelectrolyte solution is analysed. The self-consistent field equations for the configurational probability of the chain are solved numerically for different parameter values of the system including the surface and polymer charge density, the amount of adsorption and the Debye-Hückel screening length. The effect of intramolecular long range Coulombic forces on the segment density profile is examined. By coupling the numerical results with simple thermodynamic arguments, we reach exact analytical expressions for the layer thickness and define critical adsorption conditions. In general, polyelectrolytes are adsorbed into flat layers. However, under conditions of weak electrostatic screening and low surface and polymer charge densities, we expect large loops to be formed. Strong electrostatic screening does not lead to expanded conformations but causes chains to desorb.

1. Introduction.

We examine in this paper the structure of a layer formed by long polyelectrolyte chains adsorbed at the phase boundary of a solid and a polyelectrolyte solution, the surface of the solid and the polymer are supposed to carry charges of opposite sign. This is a problem of fundamental and practical interest [1].

From the theoretical side, the conformations of non-charged homopolymers and copolymers at interfaces have been extensively described. More recently, the structure of polyelectrolyte chains grafted by one end on a surface and immersed in an electrolyte solution was analysed [2-4]. In the same spirit was also examined the brush conformation of a diblock copolymer at liquid/liquid interfaces with one of the blocks being charged [5]. Analytical solutions were given for strong stretching conditions when the sum of the electrostatic and non-electrostatic fields can be equated to an overall parabolic potential [6, 7]. The situation relative to adsorption from a solution is rather different, because then, the number of segment/surface contacts depends on the magnitude of the potential between the surface and the polymer in the liquid medium and a diffuse layer is formed from the superposition of loops of different sizes. This picture cannot be understood within the context of the previously mentioned theories. Up

to now, a few attempts have been made to describe the situation resulting from spontaneous adsorption of polyelectrolytes :

i) The effect of electrostatic interactions among segments of a single adsorbed chain were treated by replacing the step length of the chain by an effective length including or disregarding non-electrostatic excluded volume effects [8, 9]. Since segment-segment interactions should be evaluated in the adsorbed state, it is questionable whether intramolecular Coulombic repulsions in the adsorbed state can be accounted *via* a renormalized segment length derived for the « free » chain in its solution state. This model is also not able to predict repulsions among segments belonging to different chains when many chains are adsorbed.

ii) The lattice theory of Roe [10] was extended to include electrical terms [11-13]. In that model, the segment concentration profile reaches asymptotically the solution concentration ; the surface layer is therefore not treated as a distinctive phase, and a model for the polyelectrolyte solution is needed. The latter was schematized as a repeating array of charged plates. Because of this, and since excluded volume effects were modelled through the Flory-Huggins formalism, this approach is likely to be useful when addressing concentrated or semi-diluted solutions. Its application to dilute solutions is questionable in so far as polymers behave then as discrete units, i.e., segments cannot be smeared out over the whole solution volume to derive thermodynamic and electrochemical properties.

iii) In the third approach, the self-consistent mean-field formulation first developed by de Gennes [14] and Richmond *et al.* [15] for the evaluation of the properties of neutral chains at an interface is used. Self-consistency of the potential is reached by complementing the equation for the configuration probability of the chain with a modified Poisson-Boltzmann equation. This theory was first applied to explore the behaviour of charged chains between plates [16] and to derive an analytical expression for the chain expansion at non-charged interfaces in the limit of weak electrostatic potentials [17].

In the present treatment, we shall follow the third approach. We suppose strong adsorption in the presence of a dilute solution. This complies with most of the experimental observations ; since an adsorbed chain has a finite fraction of its segments in the region of negative potential and because of the large number of units in the chain, the free-energy gain per chain is large and consequently strong adsorption at low solution concentration is the rule. It was indeed observed in a large number of experiments that the adsorption saturation (the plateau value in the isotherms) is reached at bulk polymer volume fractions as low as 10^{-5} (see for instance Refs. [18-20]). In most cases this corresponds to fairly dilute solutions with no chain overlapping. In modelling the interface as a distinct concentrated polymer phase in equilibrium with a dilute solution, we do not need a detailed description of the polyelectrolyte conformation in solution. It will be shown that, when the number of adsorbed polymers is fixed, only a few parameters — such as the charge density, Debye-Hückel and segment length — are needed to describe the segment density profile and to derive the layer thickness. However, not specifying the chemical potential in solution has the drawback of not being able to predict the adsorption isotherm. The surface excess Γ remains therefore here as a parameter. This quantity is usually determined experimentally from the change of the concentration of the solution at equilibrium with the adsorbate.

2. Model and formalism.

In the self-consistent field theory [21], the distribution function $G(\mathbf{r}', \mathbf{r}, N)$ for a flexible chain of N units to start at point \mathbf{r}' and to end at point \mathbf{r} is a Green function :

$$\left[\frac{\partial}{\partial N} - \frac{a^2}{6} \Delta - e^{-\beta U(\mathbf{r})} + 1 \right] G(\mathbf{r}', \mathbf{r}, N) = \delta(\mathbf{r}' - \mathbf{r}) \delta(N) \quad (1)$$

where a is the length of a segment, $\beta = (k_B T)^{-1}$ with k_B the Boltzmann constant and T the temperature, and $U(\mathbf{r})$ is the potential acting on a segment at location \mathbf{r} . For $\beta U(\mathbf{r}) \ll 1$, equation (1) can be linearized and $G(\mathbf{r}', \mathbf{r}, N)$ expanded in the spectral expansion :

$$G(\mathbf{r}', \mathbf{r}, N) = \sum_{\lambda} \varphi_{\lambda}(\mathbf{r}) \varphi_{\lambda}(\mathbf{r}') \exp(-E_{\lambda} N). \quad (2)$$

The eigenfunctions φ_{λ} and eigenvalues E_{λ} satisfy the homogeneous equation :

$$\left[\frac{a^2}{6} \Delta - \beta U(\mathbf{r}) \right] \varphi_{\lambda}(\mathbf{r}) = -E_{\lambda} \varphi_{\lambda}(\mathbf{r}). \quad (3)$$

For long chains ($N \gg 1$), the lowest eigenvalue E and corresponding eigenfunction $\varphi(\mathbf{r})$ dominates the spectral expansion.

Let the electrical charge on the chain be αe per segment, with e the elementary charge and α the charge parameter, $0 < \alpha < 1$. The amplitude $\varphi(x)$ and the reduced electrostatic potential $\psi(x)$, with x the coordinate in a direction normal to the surface, are defined by the following set of equations :

$$\frac{a^2}{6} \varphi''(x) = [\alpha \psi(x) + u(x) - E] \varphi(x) \quad (4)$$

$$\psi''(x) = -4 \pi \alpha L_B \varphi^2(x) + \kappa^2 \psi(x) \quad (5)$$

where $\psi(x)$ is the reduced electrostatic potential (i.e., the potential multiplied by $e\beta$) and $u(x)$ is the potential (in units of $k_B T$) of non-electrostatic origin. We address large surfaces, ignoring any concentration fluctuation in directions parallel to the surface. Equation (4) couples with the linearized Poisson-Boltzmann equation (5) in which the square of the amplitude $\varphi(x)$ is (when properly normalized) the segment density and

$$\kappa = (8 \pi L_B C)^{1/2} \quad (6)$$

$$L_B = \beta \varepsilon^{-1} e^2 \quad (7)$$

where L_B is the Bjerrum length, C the concentration of the electrolyte (uni-univalent electrolyte) and ε the dielectric constant.

Because of the condition $\beta U \ll 1$ needed to express $G(\mathbf{r}', \mathbf{r}, N)$ as the sum of different amplitudes, the Poisson-Boltzmann equation is also used here in its linear form which restricts of course our considerations to weakly charged systems.

The set of coupled self-consistent equations (4)-(5) were analysed within the framework of elaborated field theories [16] ; they can also be derived more simply from the free-energy F associated with a segment, see [17] :

$$\begin{aligned} \beta F = & \int_0^{\infty} u(x) \varphi^2(x) dx + \int_0^{\infty} [e^{-1} \rho(x) \psi(x) - (8 \pi L_B)^{-1} (d\psi/dx)^2] dx \\ & + \int_0^{\infty} \frac{a^2}{6} [d\varphi/dx]^2 dx + \sum_i \int_0^{\infty} [C_i \text{Ln}(C_i/C - C_i)] dx \end{aligned} \quad (8)$$

$$\rho(x) = \alpha e \varphi^2(x) + e \sum_i z_i C_i. \quad (9)$$

The successive integrals on the right hand side represent : the free-energy resulting from interactions of non-electrostatic nature, the electrostatic contribution, the entropy loss of the

chain and the entropy of mixing mobile ions. Taking $z_i = \pm 1$ and keeping the total amount Γ of segments per unit area constant,

$$\Gamma = \int_0^{\infty} \varphi^2(x) dx \quad (10)$$

the minimization of the functional F with respect to $\varphi(x)$, $\psi(x)$ and $C_1(x)$ restores equations (4)-(5).

3. Numerical solution.

The density profile $\varphi^2(x)$ was derived for different values of α , κ , Γ by numerical integration of the set of equations (4)-(5). The boundary conditions were fixed as follows :

$$\varphi(0) = 0 \quad (11)$$

$$\psi'(0) = -4 \pi L_B \sigma e^{-1} \quad (12)$$

σ is the charge per unit area of the surface. Equation (11) is the correct boundary condition to be used in the case of an adsorbing surface [22]. The confinement of the chain near the solid is in fact equivalent to an external potential which is infinite for $x < 0$ and zero for $x > 0$ (see also [9] and [21]), therefore the concentration must be zero at the surface. This is at variance with other choices [10-13].

$\varphi'(0)$ was chosen so that equation (10) was satisfied. A relation for $\psi(0)$ can be found after multiplication of the right and left sides of equations (4)-(5) by $\varphi'(x)$ and $\psi'(x)$ respectively and after computing the integrals

$$\int_0^{\infty} \frac{d}{dx} [\varphi'(x)]^2 dx, \quad \int_0^{\infty} \frac{d}{dx} [\psi'(x)]^2 dx$$

E was adjusted to ensure that $\varphi(x)$ and $\psi(x)$ converge uniformly to zero for $x \rightarrow \infty$.

APPLICATION TO CHARGED SURFACES. — $\sigma \neq 0$, $u = 0$. In this situation, attraction of the chains towards the surface occurs through long range electrical forces among surface charges and segment charges of opposite signs (in Eqs. (4)-(5), σ is taken as negative and α as positive). The surface potential is then given by the following relation :

$$\psi(0) = - [(4 \pi \sigma L_B \kappa^{-1} e^{-1})^2 - 4/3 \pi L_B (a \kappa^{-1} \varphi'(0))^2]^{1/2} \quad (13)$$

Any interactions of non-electrostatic origin are henceforth ignored. The correct term for the potential would be : $\alpha \psi(x) + v \varphi^2(x)$, v being the non-electrostatic excluded volume. We focus here only on electrostatic effects and suppose thereby $\alpha \varphi \gg v \varphi^2$. We shall come back to this point later when discussing the order of magnitude of the respective parameters.

In figure 1 are shown different curves (1), (2) and (3) which represent the calculated profile as a function of distance x for $\sigma e^{-1} = -2 \times 10^{-4} \text{ \AA}^{-2}$, $\kappa^{-1} = 120 \text{ \AA}$, $\alpha = 0.2$, $a = 4.8 \text{ \AA}$ and different adsorption values Γ : $7.9 \times 10^{-4} \text{ \AA}^{-2}$ (curve 1) ; $2.7 \times 10^{-4} \text{ \AA}^{-2}$ (curve 2) and $0.37 \times 10^{-4} \text{ \AA}^{-2}$ (curve 3). The maxima as well as the average distance L of segments defined by equation (14) are shifted

$$L = \Gamma^{-1} \int_0^{\infty} x \varphi^2(x) dx \quad (14)$$

towards lower x values as Γ decreases.

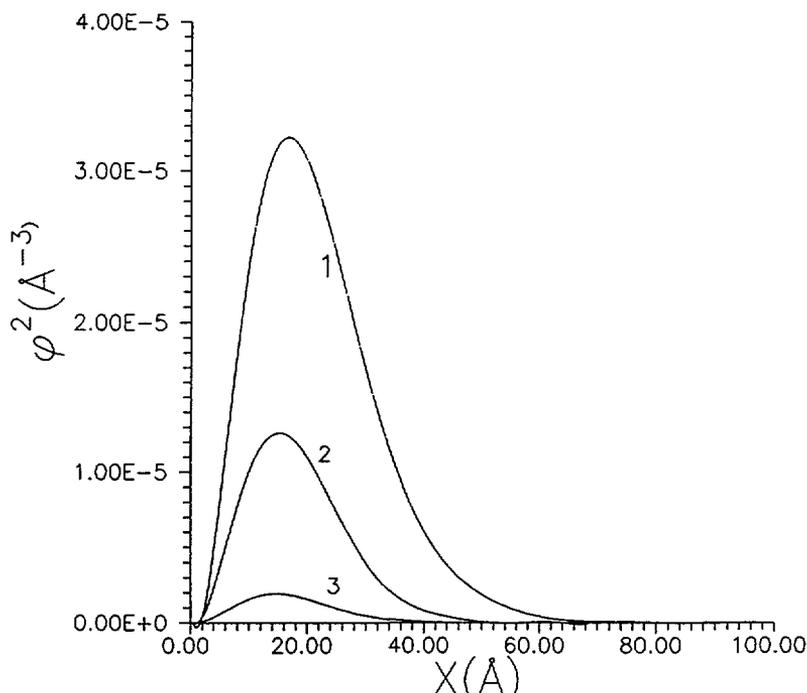


Fig. 1. — Segment density profile determined for different amount Γ of polymer units adsorbed with $\sigma e^{-1} = -2 \times 10^{-4} \text{\AA}^{-2}$, $\kappa^{-1} = 120 \text{\AA}$, $a = 4.8 \text{\AA}$, $\alpha = 0.2$: $\Gamma = 7.9 \times 10^{-4} \text{\AA}^{-2}$ (1), $\Gamma = 2.6 \times 10^{-4} \text{\AA}^{-2}$ (2), $\Gamma = 0.37 \times 10^{-4} \text{\AA}^{-2}$ (3); $E = -0.06$ (1), $E = -0.22$ (2) and $E = -0.327$ (3).

Results reported in figure 1 correspond to a value of κ^{-1} which is large compared to the thickness L ; electrostatic interactions between segments are then weakly screened and the polymer collapses into a rather flat conformation. In this situation, the charge density close to the surface is dominated by the $4 \pi \alpha L_B \varphi^2(x)$ term in equation (5). The space charge density in the vicinity of the surface increases for large Γ values and gives rise to enhanced intramolecular long-range Coulombic repulsions and consequently to more expanded conformations. The effect is however not pronounced. In an earlier approach to interpret the adsorption of a single chain, the $4 \pi \alpha L_B \varphi^2(x)$ term was neglected in equation (5) and the potential was taken to be a simple exponential: $\psi(x) = L_B \kappa^{-1} \sigma e^{-1} \exp(-\kappa x)$, [23]. With this simplification equation (4) transforms into a Bessel equation with a solution of the form:

$$\varphi(x) = J_\nu [\kappa^{-1} a^{-1} (24 \theta)^{1/2} \exp(-\kappa x/2)] \quad (15)$$

$$\theta = 4 \pi |\sigma| e^{-1} \alpha L_B \kappa^{-1} \quad (16)$$

where J_ν is a Bessel function of order ν and the eigenfunction ν is fixed by the condition $\varphi(0) = 0$, i.e.,

$$J_\nu [\kappa^{-1} a^{-1} (24 \theta)^{1/2}] = 0. \quad (17)$$

The approximated profile calculated by equation (15) and the exact profile are displayed in figure 2, parameters κ^{-1} , α , σ being the same as for curve (1) in figure 1. The omission of the polymer charges in the Poisson-Boltzmann equation brings in a difference of about 20 % on the

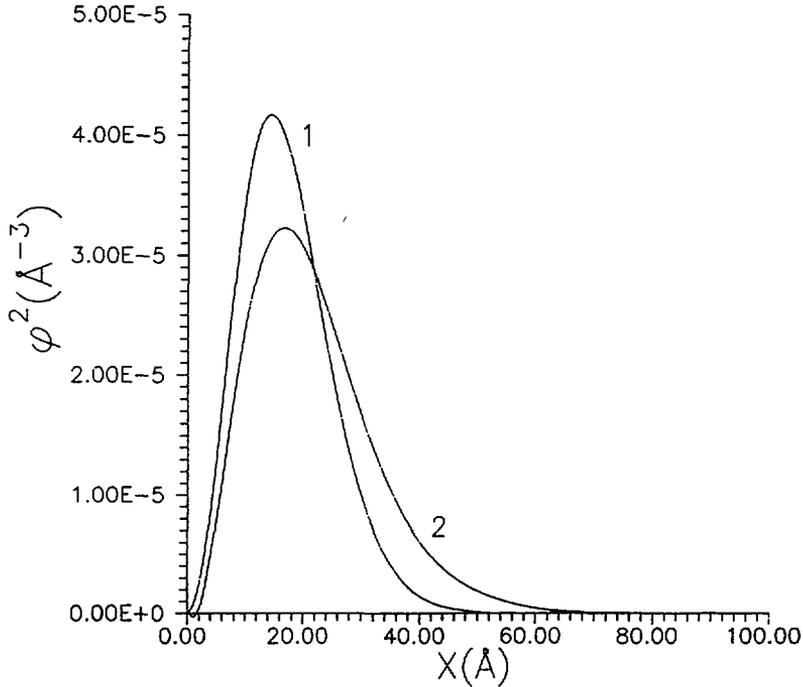


Fig. 2. — Segment density profile for $\sigma e^{-1} = -2 \times 10^{-4} \text{\AA}^{-2}$, $\kappa^{-1} = 120 \text{\AA}$, $a = 4.8 \text{\AA}$, $\alpha = 0.2$, $\Gamma = 7.9 \times 10^{-4} \text{\AA}^{-2}$ Exact profile, curve (2); profile calculated according to relation (15), curve (1).

polymer expansion. It comes out that this has a pronounced effect on the free-energy of the system as can be seen when one compares the values of E in both cases : $E = -0.34$ (curve 1) and $E = -0.06$ (curve 2). The values of E for curves (1), (2) and (3) in figure 1 are -0.06 , -0.22 , and -0.327 , respectively. Long-range Coulombic forces between polymer units contribute therefore a significant positive part to the free-energy. The Γ value of curve (1) in figure 1 corresponds to an upper limit ; increasing further Γ by 5 % leads to a situation for which no bound states exist, i.e., no negative eigenvalues which make $\varphi(x)$ and $\psi(x)$ converge exponentially to zero for $x \rightarrow \infty$, can be found. At fixed α , κ and σ , Γ is limited by an upper bound. On the experimental level, this leads to an interesting remark : suppose an experiment in which the solution concentration is increased progressively without changing the charge parameter or the electrolyte content, the adsorption is then not expected to reach « smoothly » a plateau value but rather to stop at some critical solution concentration.

It is important to note that the adsorption of one single chain was considered in reference [23]. When for a single chain in the presence of a large surface (large when compared to the polymer size), the segment-segment interactions are neglected, the distribution function in a direction parallel to the surface is Gaussian :

$$G(r', r, N) = \frac{3}{2 \pi N a^2} \exp - \left\{ 3 [(y' - y)^2 + (z' - z)^2] / 2 N a^2 \right\} \varphi_n(x) \varphi_n(x') \exp(-EN). \quad (18)$$

In reality, because of the segment-segment interactions, ψ must also be a function of coordinates y, z : $\psi \equiv \psi(x, y, z)$, and the single chain problem is therefore considerably more

involved. If we let $N \rightarrow \infty$, $S \rightarrow \infty$ with $N/S = \text{Const.}$, then the equivalence $\Gamma = N/S$ becomes correct and the one-chain problem can be treated formally along the previous lines.

It is hard to set by numerical calculations a rational to define the critical adsorption conditions precisely. To proceed further with this point we shall use simple thermodynamic arguments which will also prove useful in the derivation of an analytical expression for the thickness of the surface layer, and from which all qualitative deductions derived from the numerical solutions can be set into a more precise statement.

4. Thermodynamic arguments.

POLYMER LAYER THICKNESS AND CRITICAL CONDITIONS. — The free-energy of the layer is the sum of an electrostatic, F_e , and a conformational F_c contribution :

$$F = F_e + F_c \quad (19)$$

$$\beta F_e = \frac{1}{2} \int_0^\infty e^{-1} \rho(x) \psi(x) dx \quad (20)$$

$$\beta F_c = [\Gamma(a/L)^2 - k_B^{-1} \Delta S_i] \quad (21)$$

$\rho(x)$ is the charge density, ΔS_i is the entropy change of small ions and $(a/L)^2$ the confinement energy per segment [24]. Ignoring numerical coefficients, for the moment we derive F_e for a constant charge density ρ_0 of segments in a distance L , i.e. :

$$\beta F_e = \frac{1}{2} \int_0^L \rho_0 e^{-1} \psi(x) dx - (\kappa^2/8 \pi L_B) \int_0^\infty \psi^2(x) dx \quad (22)$$

$$\psi'' = -4 \pi L_B \rho_0 e^{-1} + \kappa^2 \psi, \quad x < L \quad (23)$$

$$\psi'' = \kappa^2 \psi, \quad x > L. \quad (24)$$

For $\kappa^{-1} \gg L$, it can be shown that the contribution of the small ions to the free-energy has only a weak dependence on L (of order $(\kappa L)^2$) and we obtain :

$$\beta F = \Gamma(a/L)^2 + \pi L_B \kappa^{-1} \alpha \Gamma [\sigma e^{-1} (1 - \kappa L/2) + 2 \alpha \Gamma (1 - 2 \kappa L/3)] \quad (25)$$

$$\left. \frac{\partial F}{\partial L} \right|_{\Gamma, \alpha, \kappa} = 0 \quad (26)$$

with

$$e^{-1} \rho_0 = \frac{\alpha \Gamma}{L} \quad (27)$$

this gives for the box-like distribution :

$$L = (2 a^2 / \pi L_B)^{1/3} (1/2 |\sigma| \alpha e^{-1} - (4/3) \alpha^2 \Gamma)^{-1/3}, \quad \kappa L \ll 1. \quad (28)$$

The following condition must be fulfilled in order that $F < 0$:

$$\alpha |\sigma| e^{-1} > (\pi L_B)^{-1} \kappa (a/L)^2 + 2 \alpha^2 \Gamma \quad (29)$$

or

$$\alpha |\sigma| e^{-1} > \kappa (\pi L_B)^{-1/3} [\alpha (\alpha |\sigma| e^{-1} / 4 - (2/3) \alpha^2 \Gamma)^{2/3} + 2 \alpha^2 \Gamma]. \quad (30)$$

Note that when $\kappa^{-1} \rightarrow \infty$, the conformational entropy of the chain is small compared to the

electrostatic free-energy and we end up with the following simple condition :

$$|\sigma| e^{-1} > 2 \alpha \Gamma . \quad (31)$$

Using correct numerical coefficients for the exact profile (numerical coefficients can be assessed from the numerical integration for situation with $L \ll \kappa^{-1}$), we obtain the expression for the average thickness L :

$$L = (2 a^2 / \pi L_B)^{1/3} (5.17 |\sigma| \alpha e^{-1} - 6.33 \alpha^2 \Gamma)^{1/3}, \quad \kappa L \ll 1 . \quad (32)$$

The thickness of the layer depends only weakly — to a power of 0.33 — on the charge density and the adsorption amount. The free-energy is however quadratic in Γ which explains the large variation of E reported in figure 1.

Values of L calculated according to equation (32) for $e^{-1} \sigma = -2 \times 10^{-4} \text{ \AA}^{-2}$, $\kappa^{-1} = 120 \text{ \AA}$ and different α and Γ values are reported in table I (L_{app} in the last column) and compared to the exact values (L_{ex} in the third column) obtained by numerical resolution. The agreement is very good — see also figure 3. As long as L is less than $0.4 \kappa^{-1}$, the difference does not exceed 3 % ; the accuracy decreases however when κ^{-1} becomes of the same order of magnitude as L .

Table I. — Average layer thickness calculated as a function of α and Γ for $|\sigma| e^{-1} = 2 \times 10^{-4} \text{ \AA}^{-2}$, $\kappa^{-1} = 120 \text{ \AA}$.

α	$\Gamma (\text{ \AA}^{-2}) \times 10^4$	$L_{\text{ex}} (\text{ \AA})$	$L_{\text{app}} (\text{ \AA})$
0.05	1.62	28.72	27.89
0.1	0.76	22.33	22.20
0.2	7.92	21.65	21.50
0.2	0.37	17.49	17.49
0.2	2.57	18.40	18.37
0.4	0.79	14.10	14.10
0.05*	4.3×10^{-4}	43.67	43.63
0.1**	1.6×10^{-3}	24.40	21.80

* Calculated for $\kappa^{-1} = 70 \text{ \AA}$, ($\kappa L \cong 0.3$).

** Calculated for $\kappa^{-1} = 500 \text{ \AA}$ and $\sigma e^{-1} = -10^{-4} \text{ \AA}^{-2}$

When the amplitude $\varphi(x)$ is calculated by equation (15), the critical adsorption energy θ_c which corresponds to the lowest eigenvalue ν of equation (17) is defined by :

$$\kappa^{-1} a^{-1} (24 \theta_c)^{1/2} = 2.404 \quad (33)$$

which imposes the following condition for adsorption to occur :

$$\alpha |\sigma| e^{-1} > (2.404 a)^2 \kappa^3 L_B^{-1/48} \pi . \quad (34)$$

This is equation (30) in which Γ is made zero and which was derived *via* a completely different route. As already emphasized, equation (34) holds only when Γ or $\alpha \rightarrow 0$. Critical conditions were also derived in reference [9]. For $\kappa \rightarrow 0$, the structure of equation (34) is preserved

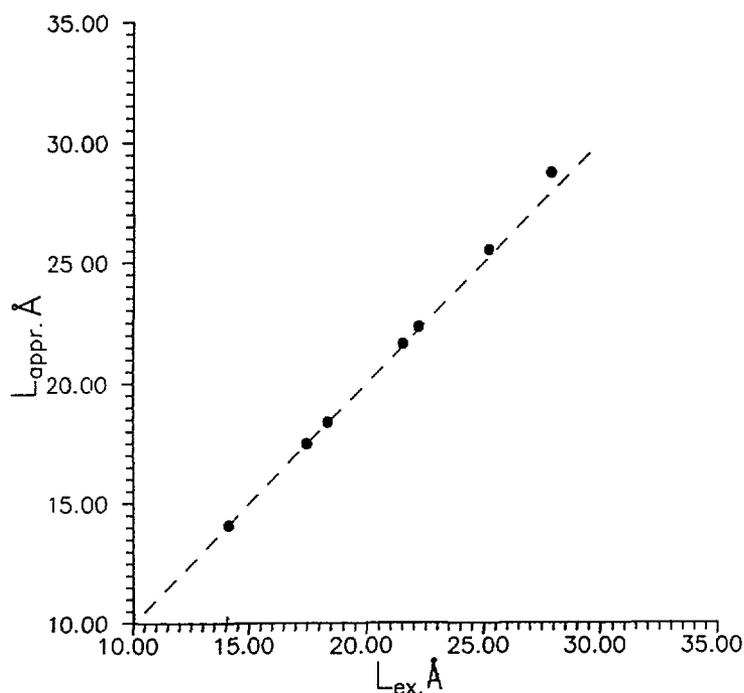


Fig. 3. — Average layer thickness: L_{appr} , calculated according to equation (32); L_{ex} , calculated by numerical integration of equations (4-5). $\sigma e^{-1} = -2 \times 10^{-4} \text{ \AA}^{-2}$, $\kappa^{-1} = 120 \text{ \AA}$, $a = 4.8 \text{ \AA}$, α and Γ values are reported in table I.

provided a^2 is replaced by the product aa_1 , a_1 being the equivalent segment length. In the limit of the unscreened case a_1 is proportional to the chain length. On the other hand, in the strong screening limit, different power laws on κ and chain length were found.

LAYER THICKNESS IN THE PRESENCE OF ELECTROLYTE. — In the previous section we have discussed the situation in which $\kappa L \ll 1$. No simple analytical expression can be derived when κ^{-1} is close to L or less than L . Numerical calculations show that L increases sharply when the screening of Coulombic forces becomes effective — see figures 4 and 5. However, the thickness of the layer cannot increase beyond a certain limit owing to the fact that below a critical κ_c^{-1} value, no finite amplitude for φ in the vicinity of the surface is found. For the parameter values used in figure 4, κ_c^{-1} is found by numerical calculation to be equal to 19.5 \AA . Equation (34) gives $\kappa_c^{-1} = 14.8$, a somewhat lower value owing to the fact that electrostatic interactions among segments are neglected in that equation.

Because the layer becomes unstable at low κ^{-1} , expanded layers cannot be reached just by decreasing κ^{-1} as could be sought at first sight. Instead, let $\kappa^{-1} \rightarrow \infty$, $\alpha\sigma \rightarrow 0$ and $|\sigma| e^{-1} \gg \alpha\Gamma$, then as can be checked by inspection of equation (32), the loop size does increase beyond limits.

5. Conclusion.

We have discussed the structure of a dense polyelectrolyte layer at the interface between a solid and a dilute polymer solution. Our hypothesis was that concentration fluctuations in the surface

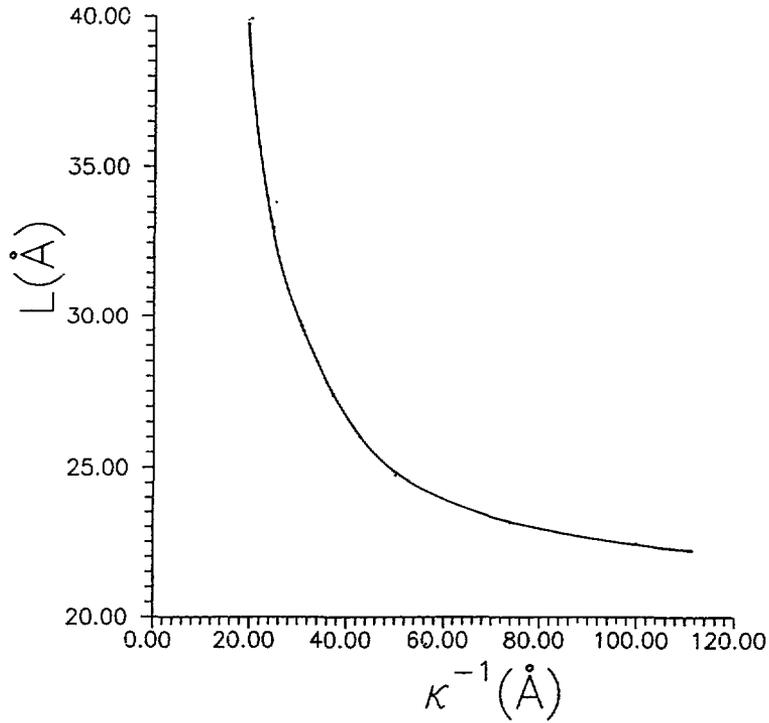


Fig. 4. — Layer thickness as a function of κ^{-1} . $\alpha = 0.1$, $a = 4.8 \text{ \AA}$, $\Gamma = 7.56 \times 10^{-6} \text{ \AA}^{-2}$

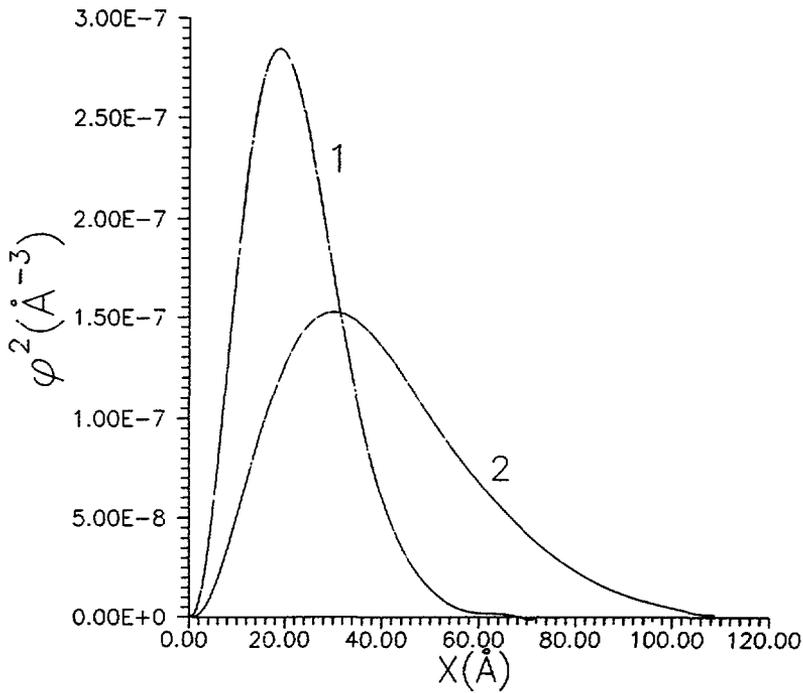


Fig. 5. — Segment density profile for two different values of κ^{-1} . $\sigma e^{-1} = -2 \times 10^{-4} \text{ \AA}^{-2}$, $a = 4.8 \text{ \AA}$, $\alpha = 0.1$, $\Gamma = 7.06 \times 10^{-6} \text{ \AA}^{-2}$. $\kappa^{-1} = 100 \text{ \AA}$ curve (1), $\kappa^{-1} = 20 \text{ \AA}$ curve (2).

layer do not contribute significantly to the free-energy. Then the self-consistent field equation can be associated with a modified Poisson-Boltzmann equation. The effect of intramolecular Coulombic forces could be assessed quantitatively after numerical integration. By complementing the numerical results with a simple scaling argument, it was possible to derive an analytical expression for the layer expansion in a direction normal to the surface under conditions of weak electrostatic screening. Critical parameter values were discussed. The adsorbed phase, though expanding in the presence of electrolyte with the inverse of the Debye-Hückel length, cannot reach large dimensions (such as those encountered for non-charged adsorbed polymers) without spontaneous desorption occurring. On the other hand, under conditions of very weak screening, large loops could possibly form, provided the surface attraction dominates the segment-segment potential in a regime of low surface and polymer charge.

One of the limitations of this work is the neglect of non-electrostatic interactions between segments. We supposed all along the condition $v\varphi^2 \ll \alpha\psi$ to be fulfilled. Let $v = 30 \text{ \AA}^3$ (good solvent conditions) and $\Gamma = 5 \times 10^{-2} \text{ \AA}^{-2}$ (which complies with experimental conditions, see f.i. Ref. [19]), then for a layer thickness of 50 \AA we obtain on the average $v\varphi^2 \cong 0.025$. The neglect of effects of non-electrostatic origin might not be warranted keeping in mind the condition $\alpha\varphi \ll 1$ which we assumed to be satisfied. Yet, it should nevertheless be kept in mind that for a large number of weakly charged polybases or polyacids, the aqueous environment behaves with respect to non-charged moieties like a poor solvent (sometimes also like a solvent below its θ point [25]). A good candidate for the present theory would be polyvinylpyridine at a pH slightly below the pH of the cloud point (the polybase precipitates at a pH of about 5 at which the charge parameter is still of the order of 10 % [26]). Weakly charged polysulfonic acids can also be ranged in this category. On the other hand the situation could be different if we think of partially hydrolysed polyacrylamide (this is a polyacid with a fraction of acrylamide units in the form of carboxylic acid, see [19]). Non-hydrolysed polyacrylamide dissolves readily in aqueous medium. The effect of dispersion forces could then play a non negligible role.

Another note of caution : we suppose no discontinuity of the dielectric constant at the interface. The role of image charges is discussed in reference [5]. As long as we address large surfaces without charge heterogeneities parallel at the interface, the question of image charges need not trouble us.

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